

ANALYSIS OF RESINS IN HIGH-ASH COAL-DERIVED PRODUCTS

F. M. Lancas, H. S. Karam and H. M. McNair
Department of Chemistry
Virginia Polytechnic Institute and State University
Blacksburg, VA 24061

INTRODUCTION

The past few years have witnessed extensive efforts to characterize coal-derived liquids. One widely used method to characterize these liquids is the SARA fractionation method by which the fossil fuel is fractionated into saturates, aromatics, resins and asphaltenes. One of these fractions, resins, is believed to play an important role in the conversion process of coal into liquid products. Liquid chromatography and solubility tests are two different approaches to the SARA fractionation. Following precipitation of asphaltenes in non-polar hydrocarbons (such as n-pentane), the deasphaltened solution can be chromatographed on silica or alumina to obtain the resins. The deasphaltened solution can also be applied to a clay column and eluted with pentane to separate resins from oils, or it can be treated with propane gas to precipitate the resins.

In this paper, resins obtained by five different methods are compared gravimetrically and by reverse phase high performance liquid chromatography. These methods are: 1) the Phillips Petroleum procedure; 2) our alternative SARA procedure; 3) fractionation by solubility; 4) fractionation by clay; and 5) our new preparative scale LC method.

Experimental

a) Preparation of resins by the different methods

The five methods investigated are conducted on the same coal, a high ash Brazilian "Mina Do Leao" coal, under the same conditions of sample preparation, extraction, and solvent evaporation. Such experimental conditions are described in detail in our previous work (1).

The Phillips Petroleum Procedure: Method 1

Ten gm coal, 60 mesh, are extracted with 100 ml hexane and the insolubles (asphaltenes) are filtered through a Whatman No. 1 cellulose filter paper. A portion of the hexane extract is applied to the top of a glass column (500 x 11 mm) dry packed with 20 gm alumina, activity I, 80-200 mesh (Fisher Scientific, Pittsburgh, PA). Saturates are eluted with 50 ml of hexane; aromatics with 75 ml of toluene; and resins with 50 ml of methanol (1,2).

The Alternative SARA Method: Method 2

This is an improved method developed in our laboratory at VPI (1). Coal is extracted with tetrahydrofuran (THF) and the unreacted coal is removed by filtration. The coal derived product, after removal of the solvent, is dissolved in 1 ml THF; then it is applied to the top of a glass column (500 x 11 mm) slurry packed with 20 gm of silica gel 60 - 200 mesh (Fisher Scientific, Pittsburg, PA). Saturates are eluted with 50 ml of hexane; aromatics with 75 ml of toluene; resins with 50 ml of methanol; and asphaltenes with 50 ml of THF.

Fractionation by Solubility: Method 3

Following extraction of the coal with tetrahydrofuran (THF) and removal of the solvent; the coal-derived product is dissolved in 2 ml of THF then treated with 80 ml of n-pentane to precipitate the asphaltenes (3). The volume of the deasphalted solution (maltenes) is reduced to 30 ml by evaporation, then placed in an ice-water bath and an excess of propane gas (99% chemically pure) is added with constant stirring, thus precipitating the resins (3). The solution is then filtered through a Whatman No. 1 cellulose filter, and the precipitate washed with propane-saturated pentane, dried, then weighed.

Fractionation by Attapulugus (florsil) column: Method 4

The deasphalted solution, as obtained in method 3, is stripped off solvent then dissolved in 1 ml of a 1:1 mixture acetone:methylene chloride. This solution of maltenes is applied to the top of a glass column (500 x 11 mm) slurry packed with 12 gm florisil, 60-100 mesh (Supelco, Bellefonte, PA). Seventy-five ml n-pentane are passed to elute "the oils", while 50 ml of 1:1 acetone:methylene chloride are passed afterwards to elute the retained "resins" in accordance with the literature (4).

New Preparative Scale LC Fractionation: Method 5

Following extraction and solvent evaporation, the THF coal derived product is dissolved in 1 ml THF, then applied to the top of a glass column (500 x 11 mm), slurry packed with 20 gm silica gel, 40-60 mesh Si-60 (EM Science, Gibbstown, NJ). Eight fractions are collected from the preparative scale column in the following order: saturates, monoaromatics, diaromatics, triaromatics, polynuclear aromatics, resins, asphaltenes and asphaltols. Table 1 shows the eluents utilized to give the best separation among the group types; the volumes used; and the fractions eluted. More details about this method can be found in the literature (5). Figures 1 and 2 show the chromatograms obtained for the non-polar and polar fractions.

TABLE 1
Eluents and Fractions Collected in the Preparative
Scale Fractionation Method: Method 5

<u>Fraction Eluted</u>	<u>Eluent</u>	<u>Volume (ml)</u>
1. Saturates	Hexane (C ₆)	40
2. Monoaromatics	Hexane (C ₆)	27
3. Diaromatics	11.5% benzene in C ₆	36
4. Triaromatics	32.0% benzene in C ₆	24
5. Polynuclear aromatics	32.0% benzene in C ₆	25
6. Resins	Benzene/(CH ₃) ₂ CO/MeCl ₂ (3/4/3)	65
7. Asphaltenes	(CH ₃) ₂ CO/THF(2/8)	60
8. Asphaltols	Pyridine	65

b) High Performance Liquid Chromatographic Separation

The analytical instrument used was a Varian Model 5020 High Performance Liquid Chromatograph. Detection was made using a Varian Varichrom Detector at 254 nm. The peaks were recorded on a Varian Model 9176 recorder. A high pressure sixport Valco valve model N-60 was utilized with a sample loop of 10 μ l. The column used was 150 x 4 mm Micropak 5 μ , RP-18. Mobile phase was a 70/30 acetonitrile/water at a flow rate of 1 ml/min. Each resins fraction, after removal of the solvent, was dissolved in THF to a concentration of 10 mg/ml. The solutions were then double filtered through 5.0 μ m Millipore filters (type LS) and finally diluted to a concentration of 0.4 mg/ml with acetonitrile prior to injection on the HPLC system.

Results and Discussion

a) Gravimetric analysis of resins

Table 2 displays a comparison of the relative distribution of resins among the five methods investigated as applied to the Brazilian coal.

TABLE 2

Relative Distribution of Resins in the Brazilian
Coal Extract Using Different Separation Methods

<u>Method</u>	<u>Wt. % Resins*</u>	<u>σ</u>	<u>% σ (RSD)</u>
1. Phillips	29.4	10	35
2. Alternative SARA	51.8	---	---
3. Fractionation by solubility	15.1	0.44	2.9
4. Fractionation by Clay	10.5	0.15	1.4
5. LC Preparative Scale	57.8	0.33	0.57

*Results from 4 repetitive runs

Table 2 shows that method 5 is by far the most reproducible system investigated. In both methods 2 and 5, resins are the major fraction in the coal-derived product. It is important to note that in methods 2 and 5 the whole THF coal extract was applied to the chromatographic column without any previous precipitation of asphaltenes (methods 1, 3, 4) or resins (method 3). The new preparative scale LC method is more complete than method 2, yielding eight discrete and pure chemical classes as has been evidenced by HPLC (see figures 1 and 2). In addition, it has a recovery of more than 94% of the loaded sample (6). The fractionation of the whole coal extract by this method yields purer fractions than those obtained by the traditional solubility fractionation, thus avoiding the contamination by co-precipitation commonly encountered in this method (1). In a different set of experiments, an asphaltenes sample (benzene soluble, pentane insoluble) from the solubility fractionation method was studied by the new method and the result showed that what seemed to be asphaltenes was in fact more than 70% resins (7).

High Performance Liquid Chromatography Analysis

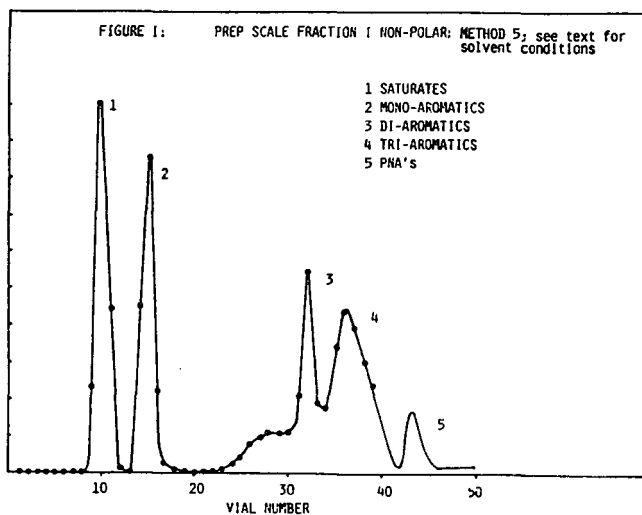
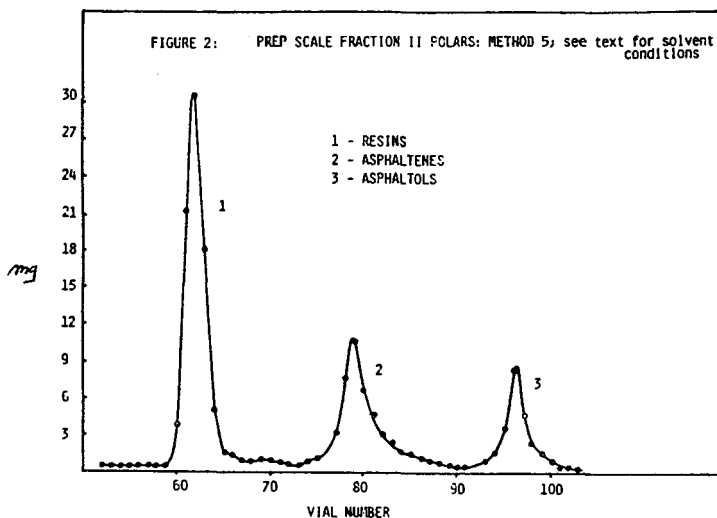
The chromatogram in figure 3 is for a standard mixture of polar compounds found in coal-derived liquids. A range of functional groups was chosen to represent many of the compound classes which could be found in coal. Structures of these compounds are shown in figure 3. Figure 4 shows a chromatogram for resins produced by method 5 while figures 5 and 6 show chromatograms for resins produced by methods 4 and 3. It is important to note that all resin solutions were chromatographed under identical conditions. Figure 3 shows that the column is very efficient. Figures 4, 5 and 6 show that the resin fraction obtained from coal by several separation procedures is still extremely complex and even better sample separation schemes need to be developed. We are continuing efforts along these lines.

Conclusion

Both gravimetric and HPLC results show that depending on the fractionation method of the coal-derived product one gets different distributions of resins. Among the different methods studied, the new preparative LC scale method seems to yield purer fractions; it produces a higher yield of sample (94%); and it is a complete method that fractionates the whole coal derived product in a single step without the inconvenience of precipitating asphaltenes or resins.

REFERENCES

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6. Lancas, F. M., Karam, H. S. and McNair, H. M., in preparation
7. Karam, H. S. Unpublished results



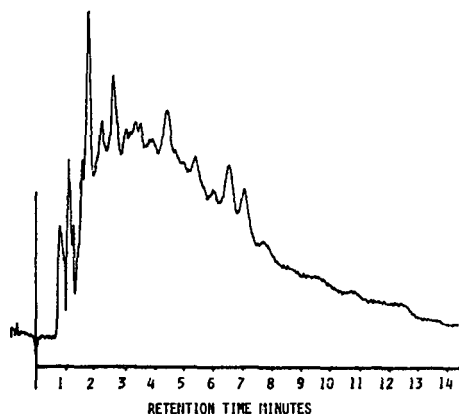


FIGURE 4: RESINS FRACTION PRODUCED BY METHOD 5
ISOCRATIC; 70/30 ACETONITRILE/WATER
2 ml/min. U.V. AT 254 x 0.05 AUFS

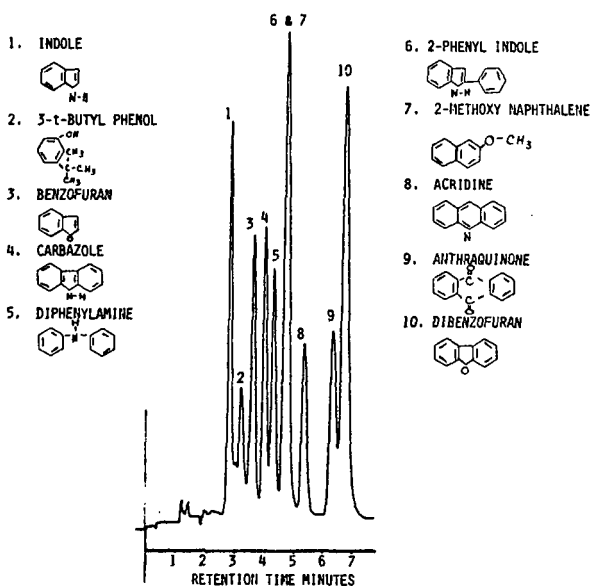


FIGURE 3: REVERSE PHASE SEPARATION OF
STANDARD MIXTURE; TEMPERATURE AMBIENT:
COLUMN 150 x 4 mm RP-18 HICOPAK 5 μ ,
FLOW RATE 1ml/min ISOCRATIC: 70/30
ACETONITRILE/WATER U.V. AT 254 nm,
0.2 AUFS

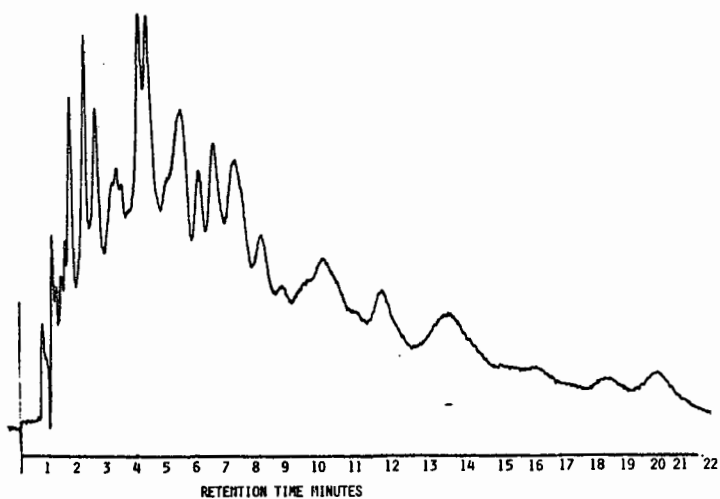


FIGURE 6: RESINS FRACTION PRODUCED BY METHOD 3; conditions same as figure 4

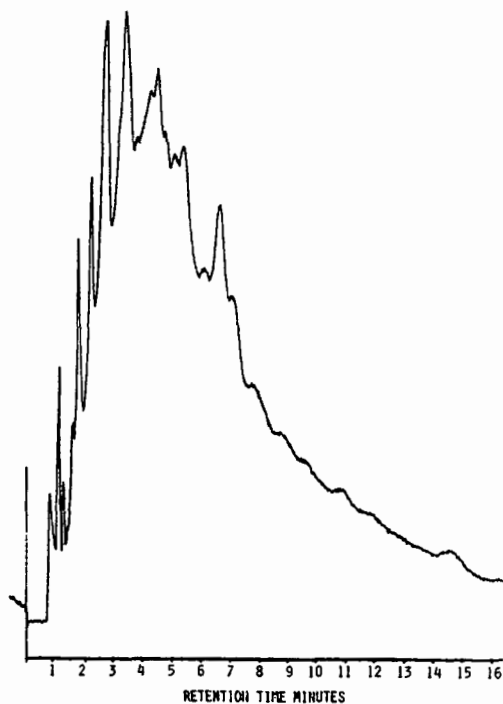


FIGURE 5: RESINS FRACTION PRODUCED BY METHOD 4; conditions same as figure 4